

# AMENDED SPECIFICATION

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## PATENT SPECIFICATION



Convention Date (Austria): May 15, 1933.

422,948

Application Date (in United Kingdom): May 14, 1934. No. 14540/34.

Complete Specification Accepted: Jan. 22, 1935.

### COMPLETE SPECIFICATION

#### Method of Producing Therapeutically and Disinfectantly Active Substances

I, DOZENT DR. FRITZ FRIGL, an Austrian Citizen, of 38, Währingerstrasse, Vienna IX., Austria, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to a process for the production of therapeutically and disinfectantly active substances. It has already been proposed, for sterilising and disinfecting purposes, to employ silver or silver compounds either alone or mechanically commixed with other metallic compounds.

Suggestions have also been made previously to convert silver or silver-containing compounds into a colloidal dissolved condition in aqueous or non-aqueous liquids such as oils, and to use these preparations for therapeutic purposes. It has further been suggested to use filter masses impregnated with silver and other metals for the purification of water, containing bacteria.

Suggestions have also been made previously to mix jelly containing arsenious anhydride with jelly containing an oxide, hydroxide or salt of an alkaline earth, noble or heavy metal, which mixture is dried, reaction taking place producing arsenites which are not soluble in water.

The present invention relates to a method of producing therapeutically and disinfectantly highly active masses which contain silver in an active form, if desired in conjunction with or applied to further substances which are themselves active, such as for example substances of oxidising action, this method yielding in every case products in which the active components are contained in perfectly uniform and extremely fine dispersion. The present invention also permits, in a simple and economical manner, of the

uniform impregnation of a large variety of carrier materials with the active substances concerned.

A process for the production of therapeutically and/or disinfectantly active substances according to the present invention consists in reacting, in an alkaline medium, a silver-ion yielding compound with a lower valency metallic compound of a metal capable of existing in more than one valency, the said metal being present as a cation in the said lower valency compound. The silver in the compounds is bound in an ionogeneous form, that is to say in a form in which it is capable of reacting with the metallic compounds which are capable of forming oxides, hydroxides, or basic salts in a number of valencies. This action of the metallic compounds on the silver compounds is preferably effected in an aqueous medium. The hydroxyl ions can be supplied by the addition of alkaline reacting substances of any kind, such as for instance alkalis, ammonia, and carbonates, but also by the employment of oxides, hydroxides, or basic salts of the silver participating in the reaction or of the metals themselves which have a number of valencies.

For example there are suitable for the carrying out of the process manganous, cobaltous, ferrous, and cerous salts on the one hand, and silver compounds for example silver nitrate on the other hand. On the reaction of these substances in an alkaline medium there result bulky but well filterable and readily washed out precipitates which consist of extremely finely divided silver and of the higher valency oxides or hydroxides of the polyvalent metals.

I have found that substances obtained in this manner have eminent bactericidal properties, and as compared with the

known silver preparations, in addition to many economical advantages possess very considerable therapeutical merits.

These products possess, in addition to the effects of the finely divided silver, the favourable properties of the thus particularly active oxygen-containing compound of the polyvalent metals employed. There is here given as an example a reaction product from manganous salt, silver nitrate, and alkali, which, after short washing with water, represents a bulky precipitate of a homogeneous mixture of manganese dioxide and silver the favourable properties of which are far better than those of a mixture of manganese and silver produced in any other manner.

Very particular advantages are provided by one form of the process according to the invention which consists in depositing the substances produced in accordance with the invention during their evolution directly upon carrier substances of a large variety of kinds.

As carrier substances there may serve, for instance in the production of disinfectant and even permanently sterile dressing and wound treating materials, fibrous matter of all kinds such as textile fibres, cotton, and fabric; further there can also be employed as carrier material substances such as animal charcoal, silica gels, bole, and other pulverulent substances which are in themselves innocuous for the present purpose, and which are also themselves capable of serving as yielders of hydroxyl ions. This can be effected either by a preliminary treatment of the carrier material with substances of alkaline reaction or by the employment of substances which themselves have sufficiently alkaline reaction; for example carbonates of the alkaline earths, oxides such as  $MgO$ ,  $ZnO$ , and others. In all these cases it is sufficient to treat the carrier material preferably with a solution of the starting materials, and then to wash out any surplus of these substances.

In many cases it is advantageous to cause the reaction to proceed in the presence of protective colloids, for example albuminous substances, vegetable mucilage, lecithins, and others. In this manner it becomes possible to produce colloidal solutions or extremely fine suspensions of the reaction products which prove efficacious as active substances for the treatment of various infectious diseases, for example gonorrhoea.

As carrier substances there can of course also be used therapeutically active substances (for example animal charcoal) which are themselves therapeutically active. The substances produced by the

present process can likewise with advantage become evolved in the presence of further therapeutically active substances known per se, whereby in many cases there are again obtained products with far better properties than when the mixtures of the substances are made only with the finished reaction products.

In those cases in which it is desired to employ the silver precipitated in accordance with the invention, without further reaction components, the latter can be separated from the silver by suitable solution reactions. For example, from a mixture of silver and manganese dioxide ( $MnO_2$ ) the latter can be readily removed by the action of hydrogen peroxide in a solution rendered acid by sulphuric acid or its compounds. The silver remains behind in an active form. With the employment of the process according to the invention the quantity of the resulting reaction products consisting of silver and higher valency metallic oxide can be accurately predetermined by apportionment of the quantity of the substance used for supplying hydroxyl ions. It is possible for example to preliminary impregnate a carrier material to be treated, such as fibrous matter, with a measured quantity of alkali. If this fibrous material be then caused to react for example with a solution of a mixture of surplus silver nitrate and manganous sulphate there will be deposited upon the fibrous material only the quantity of silver and manganese dioxide equivalent to the alkali. The sequence of commixture, as also the quantitative proportions of the individual reaction components, can also however be varied to suit the purpose in view at any one time.

The products according to the invention are also admirably well suited for the sterilizing and preserving of various substances, for example liquids such as fruit juices and more particularly non-sterile water. Liquids can be rendered practically perfectly sterile by being caused to flow over a filter mass made from the described reaction products, and preferably deposited on to a porous carrier material. It is further advantageous to impregnate the inner walls of storage vessels and containers with the reaction products according to the invention, or to place liners impregnated in this manner into other vessels and containers.

For the storage and transportation of fruit or other materials or goods liable to spoil, packing material such as wood wool, sawdust, coke, meal, and others impregnated or mixed with products according to the invention are admirably suited.

## EXAMPLES.

1. To a solution of 170 grammes of silver nitrate and 145 g of manganese nitrate ( $Mn(NO_3)_2 \cdot 6H_2O$ ) in 5 litres of water there is added caustic soda solution (for example a 15% solution) until alkaline reaction is obtained. The precipitate is drawn off, washed free of alkali, and dried at  $100^\circ C$ . There results a brown-black loose powder which consists of extremely finely sub-divided silver and quadrivalent manganese oxides in perfectly homogeneous distribution.
2. 2 litres of a 20% solution of sodium silicate is allowed to flow, under stirring into 2 litres of a solution of 40 g of silver nitrate and 34 g of manganese nitrate, and heated for an hour on the water bath. The precipitate is drawn off and washed free of alkali with hot water. The product after having been dried at  $100^\circ$  to  $110^\circ C$  and pulverisation is a greyish black powder with a silver content of about 10%.
3. Close mesh gauze is dipped into a solution of 170 g of silver nitrate and 145 g of manganese nitrate in 3 litres of water, moved to and fro in the bath for some minutes, pressed out, and placed for some minutes in normal caustic soda solution. The gauze is then well washed with water and dried.
4. 50 g of gelatine is dissolved in a litre of water, boiled for some minutes, and given the addition of a solution of 17 g of silver nitrate and 14.5 g of manganese nitrate in 500 ccs of water. Into this solution there is allowed to flow 500 ccs of normal caustic soda solution, with constant stirring. The densely black stable colloidal solution is then dialysed for several days with water, until the dialysate is of neutral reaction, and then if necessary filtered.
5. Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—
1. A process for the production of therapeutically and/or disinfectantly active substances, which consists in reacting, in an alkaline medium, a silver-ion yielding compound with a lower valency metallic compound of a metal capable of existing in more than one valency, the said metal being present as a cation in the said lower valency compound.
2. Method of carrying out the process according to claim 1, characterised in that as the metallic compound there is used a manganese salt (for example  $Mn(NO_3)_2$ ).
3. Method of carrying out the process according to claim 1 or 2, characterised by the fact that the reaction products are deposited upon carrier substances, for example fibrous substances of all kinds, fabric, pulverulent inert substances, or even therapeutically active substances.
4. A process according to claim 3, characterised by the fact that substances having themselves sufficiently alkaline reaction, for example metallic oxides, and carbonates, are employed as carrier substances, or that inert carrier substances are impregnated with substances of alkaline action.
5. A process according to any of claims 1 to 4, characterized by the fact that the reaction is caused to proceed in the presence of protective colloids (for instance albuminous substances, vegetable mucilages, lecithins, and the like).
6. Method of sterilising or preserving liquids such as fruit juices, water, fruits or other substances liable to spoil, characterised by the fact that the substances to be treated are brought into contact with the reaction products obtained according to the process of any claims 1—5.
7. The process for the production of therapeutically and/or disinfectantly active substances substantially as described.
8. Therapeutically and/or disinfectantly active substances when produced by the process according to any of the preceding claims 1 to 5 or 7.
9. Materials and goods when treated with a product obtained by the process according to any of the preceding claims 1 to 5 or 7.

Dated this 14th day of May, 1934.

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## ERRATUM

## AMENDED SPECIFICATION

No. 422,948.

Page 3, line 91, after "any" insert  
"of,"

THE PATENT OFFICE,

November 21st, 1936.